CORROSION BEHAVIOUR OF HEAT TREATED CARBON STEEL

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ABSTRACT

This thesis aims to investigate the corrosion behavior of high carbon steel at difference types of heat treatment and investigate the corrosion rate at difference temperature of heat treatment. Normalizing, water quenching and oil quenching of heat treatment were applied to the samples at selected temperature. The temperatures chosen for the heat treatment are 980 ˚C, 1015 ˚C and 1050 ˚C. Structural and mechanical properties of non heat treated and heat treated samples were determined using Vickers Hardness Test, optical microscope, Scanning Electron Microscopy (SEM). A standard micro hardness tester, equipped with a Vickers indenter and an indentation load of 500 gf was used for surface hardness measurement. The change of hardness and microstructure of heat treated AISI 1070 before corrosion and after corrosion were also observed. Electrochemical polarization measurement of the heat treated AISI 1070 were carried out by using a potentiostat. The polarization measurement of the heat treated AISI 1070 was conducted in a 3.5 % Sodium Chloride solution (NaCl). It was observed that the corrosion potential of AISI 1070 at normalized were higher than oil quenched and water quenched. Heat treatment for AISI 1070 in the 3.5 % Sodium Chloride solution (NaCl) posses a similar characteristic but different corrosion potential. The polarization curves on heat-treated AISI 1070 reveal a similar characteristic. The highest corrosion rate is non-heat treated AISI 1070 (13.96 mmpy) and the lowest corrosion rate is water quenched AISI 1070 at 1050 ˚C (0.5148 mmpy).

ABSTRAK

Tesis ini bertujuan untuk mengkaji sifat pengaratan keluli karbon tinggi pada perbezaan jenis rawatan haba dan mengkaji kadar pengaratan pada perbezaan suhu rawatan haba. Penyejukkan secara perlahan pada suhu bilik, penyejukkan dengan cepat menggunakan air dan penyejukkan dengan cepat menggunakan minyak adalah rawatan haba yang telah digunakan untuk sampel pada suhu yang dipilih. Suhu yang dipilih untuk melakukan rawatan haba adalah 980 ˚C, 1015 ˚C dan 1050 ˚C. Sifat-sifat struktur dan mekanikal sampel tanpa rawatan dan sampel dirawat haba ditentukan dengan menggunakan Ujian Kekerasan Vickers, mikroskop optik, Pengimbas Mikroskopi Elektron (SEM). Penguji kekerasan mikro, dilengkapi dengan penakuk Vickers dan beban takukan sebanyak 500 gf telah digunakan untuk ujian permukaan. Perubahan kekerasan dan mikrostruktur untuk sampel dirawat haba AISI 1070 sebelum pengaratan dan selepas pengaratan juga diperhatikan. Elektrokimia pengukuran pembelauan untuk sampel terawat haba AISI 1070 telah dijalankan dengan menggunakan potentiostat. Ukuran pembelauan potentiodinamik untuk sampel terawat haba AISI 1070 telah dijalankan dalam 3.5 % larutan Natrium Klorida (NaCl). Adalah diperhatikan bahawa potensi karat AISI 1070 untuk rawatan haba pada penyejukkan dengan perlahan pada suhu bilik adalah lebih tinggi daripada penyejukkan dengan cepat menggunakan air dan penyejukkan dengan cepat menggunakan minyak. Rawatan haba untuk AISI 1070 dalam 3.5 % larutan Natrium Klorida (NaCl) menunjukkan ciri-ciri yang sama tetapi menunjukkan potensi pengaratan yang berbeza. Lengkung pembelauan pada sampel rawatan haba AISI 1070 menunjukkan ciri-ciri yang sama. Kadar pengaratan tertinggi ialah untuk sampel tanpa rawatan AISI 1070 (13.96 mmpy) dan kadar pengaratan terendah adalah untuk sampel penyejukkan dengan cepat menggunakan air AISI 1070 pada suhu 1050 ˚C (0.5148 mmpy).

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LIST OF SYMBOLS

α	Alpha ferrite
°C	Degree Celsius
%	Percentage
b_a	Anodic Tafel slopes
b_c	Cathodic Tafel slopes
cm	Centimeter
e^-	Electrons
E	Potential
E_{appl}	Potential applied
E*corr*	Corrosion potential
i_{corr}	Corrosion current density
In	Natural logarithm
kg	Kilogram
kV	Kilovolts
kΩ	Kilo ohms
mm	Millimetre
m	Meter
mA	Milliampere
m/s	Meter per second
mV/s	Millivolts per second
R_p	Resistant potential
s	Second
V	Voltage
wt%	Weight percentage
μ	Micro
γ	Gamma ferrite
ζ	Polarization expressed

LIST OF ABBREVIATIONS

A	Area
AISI	American Iron and Steel Institute
BCC	Body-centered cubic
C	Carbon
CR	Corrosion rate
EW	Equivalent weight
d	Density
FCC	Face-centered cubic
Fe	Iron
Fe^{2+}	Iron ion
Fe_3C	Cementite
H_2O	Water
HSLA	High Strength Low Alloy Steel
HV	Hardness value
L	Liquid
M	Metal
Mn	Manganese
mmpy	millimetre per year
NaCl	Sodium Chloride
O_2	Oxygen gas
OH	Hydroxide
P	Phosphorus
Pt	Platinum
SEM	Scanning Electron Microscopy
S	Sulphur
Si	Silicon
Wt	Weight
FKM	Faculty of Mechanical Engineering
FYP	Final Year Project
UMP	Universiti Malaysia Pahang

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Corrosion can be defined as the deterioration of a material resulting from chemical attack by its environment. Most corrosion of materials involves the chemical attack of metals by electrochemical cells. By studying equilibrium conditions, the tendencies of pure metal to corrode in a standard aqueous environment can be related to the standard electrode potential of the metals. However, since corroding systems are not at equilibrium, the kinetics of corrosion reactions must also be studied. Some examples of kinetic factors affecting corrosion reaction rates are the polarization of the corrosion reactions and the formation of pasive films on the metals. Corrosion can be controlled or prevented by many different methods. To avoid corrosion, materials that are corrosion-resistant for a particular environment should be used where feasible. For many cases corrosion can be prevented by the use of metallic, inorganic, or organic coatings. The proper engineering design of equipment can also be very important for many situations, for some special cases, corrosion can be controlled by using cathodic or anodic protection system (Smitch, 2006).

Heat Treatment is the controlled heating and cooling of metals to alter their physical and mechanical properties without changing the product shape. Heat treatment is sometimes done inadvertently due to manufacturing processes that either heat or cool the metal such as welding or forming. Heats Treatment is often associated with increasing the strength of material, but it can also be used to alter certain manufacturability objectives such as improve machining, improve

formability, and restore ductility after a cold working operation. Thus it is a very enabling manufacturing process that can not only help other manufacturing process, but can also improve product performance by increasing strength or other desirable characteristics. Steels are particularly suitable for heat treatment, since they respond well to heat treatment and the commercial use of steels exceeds that of any other material.

1.2 PROBLEM STATEMENT

Carbon steel is used in large applications such as in marine, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment. Carbon steel will corrode when two chemical processes involve, which is oxidation and reduction. Oxidation is the process of stripping electrons from an atom and reduction occurs when an electron is added to an atom. Carbon steel can corrode in many media including most outdoor atmospheres. Corrosion scientists and corrosion engineers are the important people to improve the understanding the causes of corrosion or applied scientific knowledge to control the corrosion. The corrosion normally lead to spend highly cost for replacing corroded structures, for example replace a machinery or their components, such as condenser tubes, mufflers, pipelines and metal roofing, including necessary labor. Beside that, to prevent the corrosion, extra cost is needed to use corrosion resistant materials (Revie and Uhlig, 2008). Analysis on the corrosion behaviour of heat treated carbon steel has been investigated in this project.

1.3 OBJECTIVES OF STUDY

The objectives of the project that needed to be achieved are:

i. To study the corrosion behaviour of high carbon steel at differences type heat treatment.
ii. To investigate the corrosion rate at difference temperature of heat treatment.

1.4 PROJECT SCOPE

The project scopes for this project are listed below:

i. The raw material that used is high carbon steel.
ii. Sample preparation of high strength steel based on plate with dimension 15 mm in length, 15 mm width with thickness 3 mm for all sample.
iii. Every sample will quench in water, quenching in oil and normalizing at different temperature.
iv. Compositional and microstructure analysis before & after exposure to the high temperature.
v. Analysis corrosion rate by using electrochemical test.
vi. Microstructure analysis by using optical and scanning electron microscopy (SEM).
vii. Hardness test by using Vickers hardness test machine.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Corrosion is very serious problems occur on the metal and make difficult to an engineer. The corrosion happen will affect the performance especially in the industry. There are several examples that show how the corrosion cost is very high while doing the maintenance. The chemical company have to spent big money to prevent or maintenance the corrosion and the petroleum industry always also spent about million dollars per day to protect underground pipelines and another spends on painting steel to prevent rusting by a marine atmosphere.

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Non-metals are not included in the definition of corrosion. Since corrosion involves chemical changes, everyone must be familiar with principle of chemistry in order to understand the corrosion reaction because most of the corrosion happens in the world due to electrochemical. In the corrosion we can divide two types which are corrosion science and corrosion engineering. The corrosion scientist studies corrosion mechanism to improve the understanding of the causes of the corrosion and improve the ways to prevent or minimize damage caused by corrosion. The corrosion engineer is the person responsible to applies scientific knowledge to control corrosion. Loss of metal by corrosion is a waste not only of the metal, but also of the energy, the water, and the human effort that was used to produce and fabricate the metal structure in the first place. The three main reasons for the importance of the corrosion are economics, safety, and conservation.

2.2 TYPES OF CORROSION DAMAGE

Corrosion is often thought of only in terms of rusting and tarnishing. However, corrosion damage occur in other ways as well, resulting for example, in failure by cracking or in loss of strength or ductility. In general, most type of corrosion, with some exceptions, occur by electrochemical mechanism, but corrosion products are not necessarily observable and metal weight loss need to be appreciable to result in major damage (Revie and Uhlig, 2008).

The corrosion behaviour of engineering materials is influenced by many factors such as:

i. Chemical composition and microstructure of the metal
ii. Chemical composition of environment
iii. Physical parameters such as temperature, convection, irradiation , etc.
iv. Mechanical forces including tensile stresses, shocks or friction

Because the corrosion behaviour of metals is governed by complex interaction involving many parameters, it manifests itself in numerous often unanticipated forms. The corrosion resistance of a given metal is not an intrinsic property of that metal, but a system property. The same metal may rapidly corrode in a certain environment while under different conditions it is stable. From a more fundamental point of view, the corrosion resistance of metals is essentially determined by the reactivity of the metal-environment interface. Certain types of corrosion damages found in practice present a characteristic appearance that provides a hint as to their probable origin a mechanism (Landolt, 2007).There are several types of corrosion, depending on the metal, corrosive agent, geometry and environment.

i. Uniform corrosion: Uniform corrosion is a loss of material distributed uniformly over the entire surface exposed to the corrosive environment. Metals in contact with strong acids are sometimes subject to uniform corrosion

ii. Galvanic corrosion: Galvanic corrosion also called bimetallic corrosion, result from the formation of an electrochemical cell between two metals. The corrosion of the less noble metal is thus accelerated

iii. Crecive corrosion: Crecive corrosion is caused by a difference of oxygen availability between two sites on a passive metal that leads to the formation of an electrochemical cell. A selective attack within cracks and at other sites of poor oxygen acces is frequently observed

iv. Pitting corrosion: Pitting corrosion is observed on passive metals in presence of certain anions (in particular chloride) when the potential exceeds a critical value. This process typically produces cavities with diameters on the order of several tens of micrometers.

v. Intergranular corrosion: Intergranular corrosion is a selective attack of grain boundaries. Often, it is related to thermal treatments that lead preferred precipitation of phases at grain boundaries.

vi. Selective corrosion: Selective corrosion also called selective leaching or dealloying implies the selective dissolution of one of the components of an alloy that forms a solid solution. It leads to the formation of a porous layer made of the more noble metal.

vii. Erosion corrosion: Erosion corrosion is the result of an electrochemical reaction combined with a material loss by mechanical wear due to impingement of solids or a fluid.

viii. Stress corrosion cracking: stress corrosion cracking is result from the combined action of corrosion and of mechanical stress. It manifests itself by crack information at stress levels well below the ultimate tensile strength of material.

Eight types of corrosion damage are shown as in Figure 2.1.

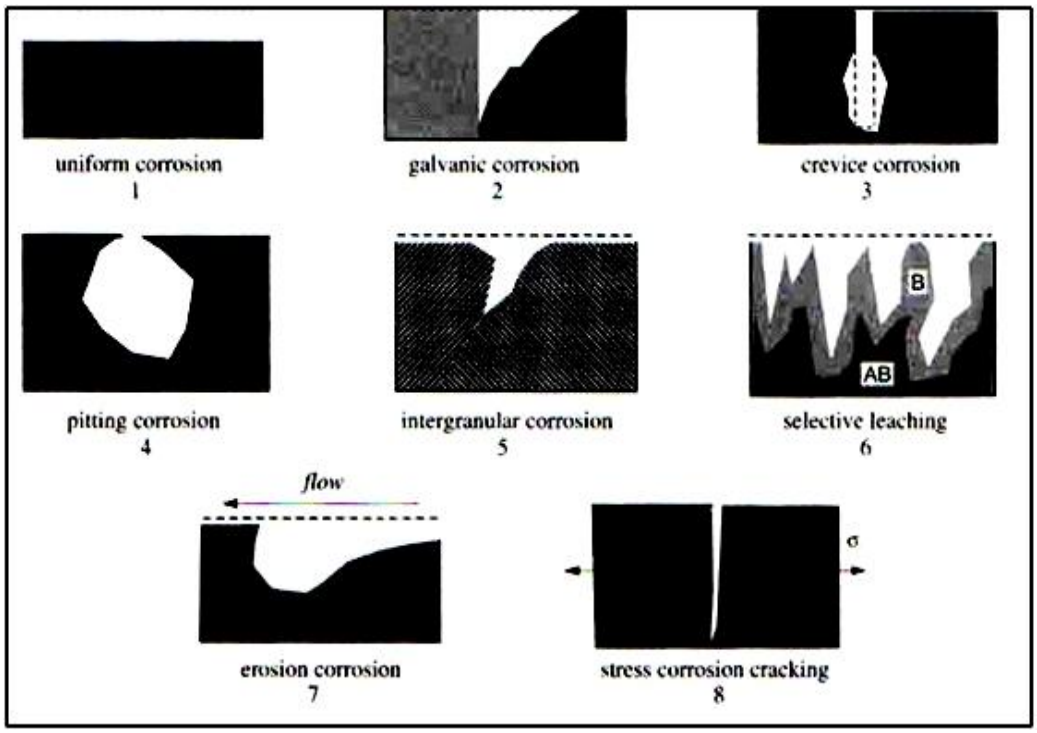


Figure 2.1: Eight types of corrosion damage

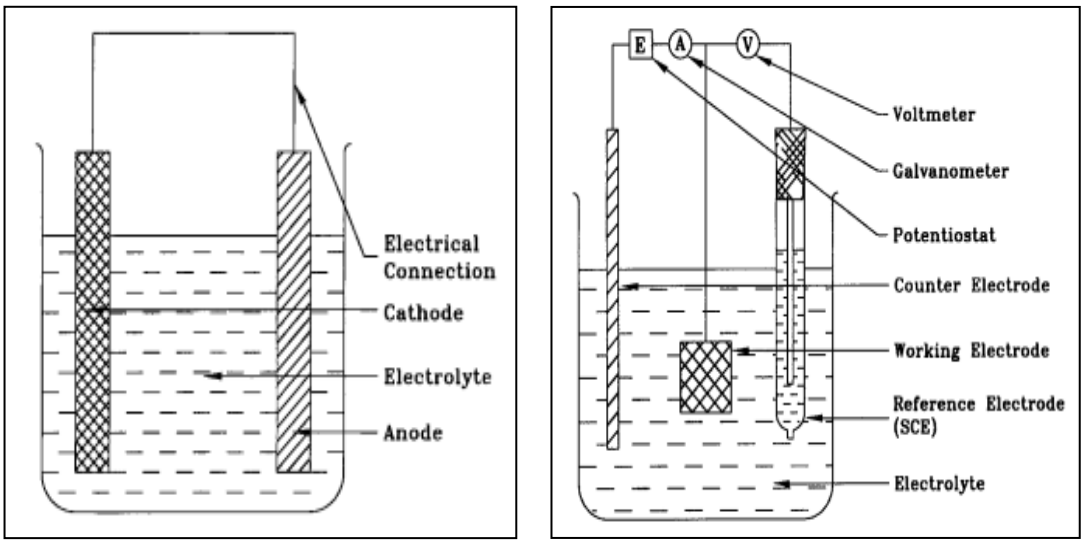
Source: (Landolt, 2007)

2.3 CORROSION CONCEPTS

Corrosion can be defined as degradation of quality and properties in a material due to the chemical reaction between the components of the material and the surrounding during electrochemical process. Electrochemical process is general process which requires the presence of an anode, a cathode, an electrolyte, and an electrical circuit in order to active the reaction.

First, the metal at the anode was dissolved and the electrons were produced from the anode as shown in Figure 2.2. The number of electrons produced was depends on the type of the metal was used. After the electrons were produced at the anode, the corrosion current was generated by the electrons and the electrons were transferred to the cathode through the electrolyte as a transfer medium. Eq. (2.1) shows that the general reaction that occurs at the anode.

$$M \rightarrow M^{n+} + e^{-} \quad (2.1)$$



(a) **(b)**

Figure 2.2: The basic corrosion cell: a) Schematic of basic wet corrosion cell, b) schematic of electrical circuitry for Polarization measurement

Source: (Tavakkolizadeh and Saatdarmanesh, 2001)

The reaction at the anode shows that a loss of electrons, or oxidation as clearly shown in Figure 2.2. The electrons produced at the anode were flow to the cathode through the electrolyte which initiates a reaction to occur at the cathode. The reaction in cathode was depends on the medium of transfer which can be divided into three groups which are acidic solution, alkaline solution and neutral solutions. All of these reactions in each solution involve a gain of electrons and a reduction process which occurred at the cathode as shown in Eq. (2.2) which in neutral solution. If the medium is in alkaline and neutral aerated solutions, the predominant cathodic reaction was shown in Eq. (2.2) .There is an important consideration when the reactions at cathode and anode were generated which is the number of electrons produced at the anode must equal the number of electrons gained at the cathode since there can be no net gain or loss of electrons (Tavakkolizadeh and Saatdarmanesh, 2001).

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH^{-}) \quad (2.2)$$

For example, if iron (Fe) was placed at the anode which exposed to aerated, corrosive water, the anodic reaction was shown in Eq. (2.3) which oxidation was occurred. However, at cathode, reduction of oxygen was occurred as shown in Eq. (2.1) .Based on the Eq. (2.3), two electrons were produced during the reaction at anode. However, based on Eq. (2.2), four electrons were required in order to balance the reaction at cathode.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{2.3}$$

Based on the concept of reaction, the number of electrons produced at the anode must equal the number of electrons gained at the cathode since there can be no net gain or loss of electrons. Thus, the anodic reaction was modified and shown as Eq. (2.4) while the cathodic reactions would be similar with previous equation. Finally, an overall oxidation-reduction reaction was shown in Eq. (2.5) which summarized the oxidation-reduction reaction occurred at the cathode and anode.

$$2\,Fe \rightarrow 2Fe^{2+} + 4e^{-} \tag{2.4}$$

$$2Fe + O^{2} + 2H_2O \rightarrow 2Fe^{2+} + 4(OH^{-}) \tag{2.5}$$

However, after the dissolution at anode, the ferrous ions or known as Fe^{2+} generally oxidize to ferric ions (Fe^{3+}) as shown in Eq. (2.6) and these will combine with hydroxide ions (OH^{-}) formed at the cathode to give a corrosion product called rust (FeO(OH), $Fe_2O_3 \cdot nH_2O$ or $Fe(OH)_3$)as shown in Eq. (2.7) and Eq. (2.8). The important issue to remember is that anodic dissolution of metal occurs electrochemically while the insoluble corrosion products are formed by a secondary chemical reaction as shown in the equation below.

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-} \tag{2.6}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+} \tag{2.7}$$

$$Fe(OH)_3 \rightarrow FeO(OH) + H2O \tag{2.8}$$

2.4 CARBON STEEL

High strength, low alloy (HSLA) steels derive their name from their higher strengths relative to plain low-carbon steels with nominal ferrite pearlite microstructure.

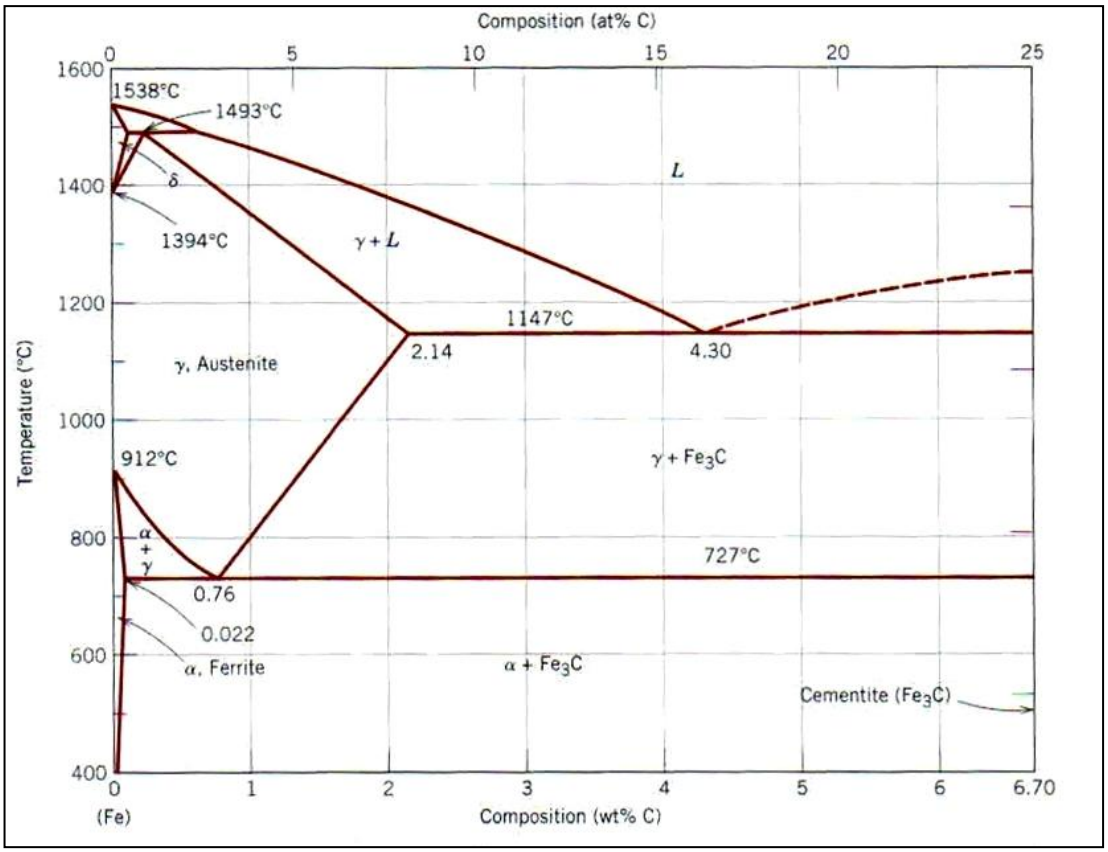


Figure 2.3: The iron-iron carbide phase diagram

Source: (Callister and Rethwish, 2008)

2.4.1 The iron-carbon system

Pure iron when heating experiences two changes in crystal structure before it melts. At room temperature the stable form is called as ferrite or α iron has a BCC crystal structure. Ferrite experiences a polymorphic transformation to FCC austenite, or γ iron, at 912 °C. This austenite persists to 1394 °C, at that temperature the FCC

austenite reverse back to BCC phase which is δ ferrite. It finally melts at 1538 °C. All these changes occur along the left vertical of the phase diagram.

Cementite is formed when composition extend only to 6.7 wt% C. The iron-carbon system may be divided into two parts which is iron-rich portion as in figure and the others are pure graphite for compositions between 6.7 wt% and 100 wt%. Carbon is an interstitial impurity in iron and form a solid solution consist of α and δ ferrite also with austenite. Small concentrations of carbon are soluble in the BCC α ferrite and the maximum soluble is at the 0.22 wt% at 727 °C. The austenite, γ when alloyed with carbon alone is nit stable below 727 °C. The maximum solubility of carbon in austenite is at 2.14 wt% which is occurring at 1147 °C. Phase transformation involving austenites are very important in the heat treating of steels (Callister and Rethwish, 2008).

When the solubility limit of carbon in α ferrite is exceeded below 727 °C the cementite will be formed (Fe_3C) at composition α + Fe_3C phase region. Cementite is brittle and very hard. At 4.3 wt% C and 1147 °C eutectic exist for the iron-iron carbide system. The eutectic reaction for the iron-iron carbide system is shown as in Eq. (2.9).

$$L \longrightarrow \gamma + Fe_3C \text{ (Cooling)} \tag{2.9}$$

The liquid solidifies and will form austenite and cementite phases. The subsequent cooling to room temperature will make additional phase changes. The eutecyoid point exists at composition 0.76 wt% and temperature of 727 °C. The eutectoid reaction for the iron-iron system may represent as in Eq. (2.10) below.

$$\gamma \text{ (0.76 wt\% C)} \longrightarrow \alpha \text{ (0.022 wt\% C)} + Fe_3C \text{ (6.79 wt\% C)} \quad \text{(cooling)} \tag{2.10}$$